

**The Current and Future Environmental Role of Atmospheric Methane:
Model Studies and Uncertainties**

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Concern over increasing levels of methane in the atmosphere centers on its radiative and chemical properties. Methane absorbs terrestrial infrared radiation and contributes to the greenhouse effect. Effects on other greenhouse absorbers (e.g., O₃, H₂O and CO₂) as the result of its oxidation must also be considered. These indirect effects have made the quantification of the total climatic effects of chemically active gases, such as CH₄, much more difficult than if direct radiative effects are considered alone. The oxidation of methane also exerts a controlling influence on atmospheric OH levels and is a major source of carbon monoxide. The variations in OH induced by changing CH₄ levels feed back onto the lifetime of methane and the abundance of CO (Sze, 1977; Chameides et al., 1977). However, there is a shortage of intercompared model results documenting the effects of CH₄ and nonmethane hydrocarbon (NMHC) additions on tropospheric OH levels. Most analyses to date have relied on analyses of gas phase reaction sequences for methane

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oxidation (e.g., Crutzen, 1987, 1988), without considering the numerous feedbacks on atmospheric chemistry. More complete modeling studies are needed because OH levels also depend on the emissions of CO, NMHCs and NO_y (NO_x + NO₃ + 2N₂O₅ + CH₃CO₃NO₂ (PAN) + HNO₃ + HNO₄ + ClNO₃ + NO₃), where NO_x is NO + NO₂ and NO_y and NX are interchangeable terms. Furthermore, analyses which simulate the role of climate in controlling CH₄ emissions from various natural sources (e.g. wetlands) are critical for attempting to predict the response of atmospheric methane levels to future climate change.

1. Calculation of Tropospheric OH Levels

The major sink for methane involves reaction with hydroxyl (OH) radicals in the troposphere (~ 90%), followed by reactions with stratospheric OH (~ 7%), chlorine atoms and singlet atomic oxygen (e.g., Lelieveld et al., 1992). Accurate calculations of OH fields are necessary, because the calculations of the total methane sink are used to constrain estimates of the total source strength of methane (Fung et al, 1991; Tie and Mroz, 1992; Khalil and Rasmussen, 1990). The accurate calculation of globally averaged OH values for use in budget studies requires knowledge of the spatial distribution of a number of species such as O₃, H₂O, CO, CH₄ and NO_x. A number of calculations of OH radical distributions in the atmosphere were presented at the Workshop. Calculations were based on a variety of one-, two- and three-dimensional models. The one-dimensional models only consider

vertical variations of horizontally averaged quantities. Such an approach is valid provided constituents are well-mixed horizontally or if horizontal transport can be neglected compared to vertical transport. This is not the case for many short-lived species in the atmosphere, especially for nitrogen oxides whose sources are highly heterogeneous. Some improvement can be achieved using hemispherical or semi-hemispherical domains, which makes some allowance for spatial variations in short lived species (e.g. NO_x and CO). An alternative approach is to consider the chemistry of chemically coherent regions separately in a one-dimensional framework, (Thompson et al., 1990). Two-dimensional models consider latitudinal variations while averaging emissions zonally (around a latitude belt). However, the short atmospheric lifetime of NO_x (about a day or two) insures that there will be large variations around a latitude belt, since the zonal mixing time is of the order of two weeks. Finally, three-dimensional models consider the full three dimensional nature of atmospheric motions and distribution of sources, but there are still questions about the adequacy of the grid resolution necessary to describe the variability of NO_x . Results presented at the workshop allow intercomparisons of the predictions of globally averaged OH levels produced by these different classes of models. These differences can be interpreted in terms of model dimensionality and grid spacing, amount and distribution of emissions, and uncertainties in the chemical kinetics data used. Values for tropospheric mean OH

levels determined by models presented at the workshop are shown in Table 1. These values are simple volume averages over the troposphere and also represent annual averages. The "hemispheric" one dimensional models are formulated for both the northern and southern hemispheres and include interhemispheric transport. The model based on chemically coherent regions is as mentioned earlier. In general, the model results all agree to better than a factor of two. Within specific classes of models, differences are more directly related to the chemical kinetics included, methods for diurnal averaging and for radiative transfer and the choice of boundary conditions, particularly for nitrogen oxides. Further work is needed to quantify and fully understand the roles of all these factors.

All modeling studies report the strong dependence of OH levels on assumed NO_x and CO levels. The relation with NO_x levels is complex, because OH levels are suppressed at very high NO_x levels (1 ppb or greater), characteristic of source regions, whereas in regions characterized by lower NO_x levels the reverse is true. At high NO_x levels the termolecular recombination reaction of NO_2 with OH to form HNO_3 is a major sink for OH and the subsequent loss of HNO_3 from the atmosphere represents a net loss for HO_x ($\text{OH} + \text{HO}_2$) radicals. Hence, OH levels tend to decrease with increasing NO_x . At lower NO_x levels this reaction decreases in importance for controlling the abundance of OH because other reactions dominate. In this regime, the recycling of HO_2 to OH by reaction with NO results in an increase in

calculated OH with increasing NO_x (Hameed et al., 1979; Logan et al., 1981). At levels of $\text{NO} > 10$ ppt, or $\text{NO}_x > 30$ ppt, the oxidation of CO , CH_4 and NMHCs tends to increase OH, whereas at low NO_x levels, their oxidation tends to consume OH (e.g., Logan et al., 1981; Crutzen, 1988; Thompson et al., 1989); Wuebbles and Tamarais, this volume). The large degree of heterogeneity of NO_x sources, coupled with its relatively short lifetime, results in calculated NO_x levels which are much higher in source regions than outside. Major source regions for NO_x are located in northern mid latitudes, where the dominant source is fossil fuel combustion and in the tropics where the major source of NO_x is biomass burning (e.g., Dignon and Penner, 1991). On the other hand, large areas of the world's oceans in the tropics and southern hemisphere are characterized by very low levels of NO_x .

Kanakidou and Crutzen (1992) conducted a study of the effects of zonally averaging emissions of NO_x and NMHCs on globally averaged OH levels in a three-dimensional model. OH levels computed using a longitudinally uniform distribution of emissions in the model were substantially higher near the surface in latitude belts where there are major NO sources, such as in northern mid-latitudes and in the tropics and 14% higher in the global average than using a ($10^\circ \times 10^\circ$) longitudinally varying distribution of emissions. The overall result was a 20% overestimate in the net destruction rate for the case of the zonally uniform emissions. Zonal averaging overestimates NO_x and NO_y (NX) levels over background areas (the oceans and remote

continental areas) whereas NO_x levels over less widespread source regions (industrialized areas of the Northern Hemisphere and tropical areas of active biomass burning) tend to be underestimated. It seems clear that these differences in the calculated OH levels have implications for the applicability of two-dimensional models to global problems and should be borne in mind when making predictions of future change in tropospheric composition. It may be that appropriate averaging techniques, such as prescribing correction factors to zonally averaged reaction rates and species abundances or incorporating modules to transform NO_x to other forms (such as PAN) at source latitudes in two-dimensional models, could be developed to provide a better comparison with three-dimensional results. Indeed, there may be more similarities in the behavior of one- and two-dimensional models, in this regard, than with three-dimensional models because the characteristic chemistry of NO_x and OH in source regions has already been averaged out in two-dimensional models. It should be noted that problems related to the dimensionality of models and grid spacing are not really independent, since the same effects should be seen within three-dimensional models as the horizontal resolution is varied.

The discussion given above refers only to differences between models based on their formulation not to differences based on uncertainties in their chemical kinetics data bases. There are also inherent uncertainties in calculations of OH due to imprecisions in the rate coefficients, UV absorption cross

sections and quantum yields used in models (NASA/JPL, 1990). For example, where NO_x levels are relatively high, the computed uncertainty in a one-dimensional model calculation of boundary layer OH due to kinetics imprecisions as specified in the standard kinetics data base (NASA/JPL, 1990) is as high as 70% (Thompson and Stewart, 1991). If fairly accurate measurements of O_3 , CO and NO_2 are available to constrain the model calculations of OH levels, the uncertainty in OH can be cut to 20%. In regions characterized by lower levels of NO_x , kinetics uncertainties introduce ~20% into the calculation of boundary layer OH. Averaging over regions that differ in NO_x emissions suggests that a typical estimate of global OH has an uncertainty of about 25% due to imprecisions in the rate coefficients for reactions used in most photochemical models (Thompson and Stewart, 1991). The largest uncertainty comes from ozone photodissociation to $\text{O}(^1\text{D})$, the initial precursor for OH formation in the troposphere. The treatment of clouds in model radiation routines is a major source of uncertainty in calculating the photolysis of ozone and other photochemically active species in a given model and of differences among model calculations of OH radical concentrations.

A further, perhaps important, uncertainty in understanding the atmospheric effects of methane oxidation arises from heterogeneous reactions of the radicals involved in the CH_4 oxidation chain, especially for CH_3O_2 , in cloud droplets, (Lelieveld and Crutzen, 1990). A critical question concerns the

fractional yield of formic acid which can be rained out, thereby reducing the yield of H_2CO , H_2 and CO from methane oxidation. The neglect of OH and HO_2 scavenging (also O_3) may introduce uncertainties into calculation of gas-phase concentrations. The possible heterogeneous conversion of labile NO_x reservoirs, such as N_2O_5 , into soluble species such as HNO_3 , tends to shift the partitioning of NO_y away from NO_x , thereby affecting the overall level of OH radicals and ozone formation.

Apart from direct calculation based on kinetic data and data for species abundances, OH values appropriate for estimating lifetimes of CH_4 and other long lived species have also been derived from the simulation of gases such as methyl chloroform (Khalil and Rasmussen, 1984; Prinn et al., 1987). Current simulations of the distribution of CH_3CCl_3 yield globally averaged OH concentrations of $8.1 \pm 0.9 \times 10^5 / \text{cm}^3$, (Prinn et al., 1991) and an increasing trend for OH of $1 \pm 0.8\%$ per year (Prinn et al, 1992). Although this method is highly useful, it is not completely free of uncertainties, since its success does depend on accurate values for rate coefficients for reaction with OH and on accurately knowing source strengths and additional loss processes. Recently it has been established that there may be an oceanic sink for CH_3CCl_3 (Butler et al. 1991) which may require downward revisions of previous values of OH of from 5 to 11%.

There are a number of sources of uncertainty involved in assessing the effects of future increases of methane in the atmosphere. Predictions are highly sensitive to the total levels

of NO_x and CO chosen and their future trends. Furthermore, there are also uncertainties in the prediction of penetrating UV-B radiation due to changes in stratospheric ozone (Liu and Trainer, 1988; Thompson et al., 1989; Thompson, 1991; Madronich, 1992) and in feedback processes from global warming, e.g. changes in cloudiness and tropospheric H_2O . In particular, models that have high globally averaged NO_x levels will tend to systematically overestimate globally averaged OH as methane levels increase. This in turn may lead to a systematic underestimate of the atmospheric lifetime and subsequently to an underestimate in the rate of increase of CH_4 concentrations for a given scenario of future methane emissions (Guthrie and Yarwood, 1991). Because of the complex set of chemical interactions involving CH_4 , NO_x , O_3 and OH, it is inappropriate to prescribe the evolution of OH levels independently from the NO_x growth scenario used in calculations of the impact of anthropogenic activities on future atmospheric composition.

2. Assessment of Climatic Effects of Methane

The concept of Greenhouse Warming Potentials (GWPs) has been introduced to assess the role of methane relative to CO_2 in the global warming problem (IPCC, 1990). As mentioned earlier, the total climatic effect from increasing methane also includes a number of indirect effects arising from its oxidation products, such as CO_2 and stratospheric H_2O . The effects on tropospheric ozone are more complex with possible production in

some regions and destruction in others, depending on the local NO_x level. These effects should also include feedbacks on OH levels and hence on the lifetime of methane itself. Estimates of Greenhouse Warming Potentials (GWPs), e.g. by Rodhe (1990), IPCC (1990), Bruhl (1992) have attempted to include these indirect effects.

$$GWP = \frac{\int_0^T \Delta Q_x(t) R_x(t) dt}{\int_0^T \Delta Q_{\text{CO}_2}(t) R_{\text{CO}_2}(t) dt} \approx \sum_i \frac{\int_0^T Q_{x_i} e^{-\nu_r t} R_{x_i} dt}{\int_0^T Q_{\text{CO}_2} e^{-\nu_r t} R_{\text{CO}_2} dt}$$

where T is the time following the unit pulse input at $T=0$, ΔQ the change in radiative forcing per unit increase in methane concentration; the summation is given over the direct and indirect effects (Wuebbles and Tamaraesis, this volume). However, while better than considering the radiative forcing from various greenhouse gases alone, there are still a number of difficulties to be overcome in developing a suitable definition for Greenhouse Warming Potentials. The decay of a CO_2 perturbation is too complex to be described by a single lifetime (Maier-Reimer and Hasselmann, 1987; Rodhe, 1990). The above equation is often applied by using a constant lifetime for methane. However, the lifetime of CH_4 may change with the scenario considered for future growth of CH_4 , CO and NO_x emissions because of feedbacks involving changing CH_4 , CO and NO_x concentrations on atmospheric OH levels. The radiative forcing terms can also change with time because of spectral overlap between absorption bands of greenhouse gases (e.g., CH_4 , H_2O and N_2O).

The generally used approximation for the decay of the pulse, $e^{-t/\tau}$ with a fixed lifetime, τ , is therefore not appropriate in many cases. To estimate indirect effects more accurately, a coupled chemistry-climate model could be used. A better way than assuming a constant decay of direct and indirect radiative forcing may be to superimpose an emission pulse to different scenarios and calculate the decay of the radiative forcing perturbation from a coupled chemistry-climate model (Bruhl, 1992). Obviously, because a calculated GWP for methane will be scenario dependent, a single number for the GWP of CH_4 is not enough, apart from any questions about model uncertainties. Instead, a range must be used which brackets extreme cases. Two cases, which demonstrate this point, are considered in Bruhl (1992); IPCC scenario B (see Harriss et al., this volume) and a case with constant background CH_4 concentration and CO and NO_x fluxes. For an integration time of 50 years, the GWP in the IPCC scenario was about 30% larger than in the second case and, of course, as the integration time in the calculation is increased the uncertainty in the resulting GWP also increases.

3. Climatic Feedbacks on Methane Sources

Future climate warming resulting from the addition of greenhouse gases to the atmosphere could also feedback onto natural sources of methane, quite apart from any human mitigation efforts. The primary factors controlling biogenic methane production in terrestrial environments are soil temperature, moisture, the availability of carbon substrates, oxygen (methane

is only produced in the absence of oxygen) and microbial populations. The interaction of atmospheric variables with soil climate and methane production dynamics is illustrated with a simplified schematic model in Figure 1. The number of potential positive and negative methane responses to climate variables is sufficiently large that it is beyond the capability of current state-of-the-art models to accurately calculate methane source feedbacks to climate variability at regional or global scales. Most studies to date have only considered the influence of temperature, arising, e.g., from global warming on methane emissions (e.g., Hameed and Cess, 1983; Harriss and Frolking, 1991). Guthrie (1986) proposed that increased photosynthesis from enhanced atmospheric carbon dioxide levels would be coupled with increased inputs of organic detritus to methanogenic environments and subsequent rates of methane emissions to the global atmosphere. Lashof (1989) has presented a qualitative summary of some of the feedback processes that may influence future concentrations of methane and other trace gases.

Advances in understanding the response of methane emissions to global warming will require a combination of field, laboratory and modeling studies. The field and laboratory studies will have to define the response functions of methanogenesis to each individual soil parameter influenced by climate variability. For example, Livingston and Morrissey (1992) have examined the interannual variability of methane emissions from Alaska arctic tundra and have pointed out the potential importance of this sort

of study for assessing the role of CH₄ emissions in climate change. Modeling studies will have to provide the framework for determining the net effect of the numerous atmospheric-biospheric interactions which interact to determine methane production and emissions (Figure 1).

Further insight into the response of methane fluxes to climate change can be obtained by examination of the ice core record of atmospheric methane variations from the Last Glacial Maximum (LGM), when globally averaged surface temperatures were about 5°C lower than today. Although methane levels during the LGM were approximately 0.35 ppm (e.g., Raynaud and Chappellaz, this volume), this does not necessarily mean that the sources of methane were a factor of five lower than today. Variations in the atmospheric sink through reaction with OH radicals must also be considered (Valentin, 1990; Pinto and Khalil, 1991; Thompson et al., 1992) and reconciled with estimates of source strengths during the LGM (Chappellaz et al., 1992). The model studies, mentioned above, calculated OH levels during the LGM about 30-50% higher than today. However, when the effects of lower temperatures on the rate coefficient for reaction of CH₄ with OH during the LGM are considered, it can be seen that an even greater fraction of the methane variations seen in the ice core record are source driven.

Chappellaz et al. (1992) propose that most of the reduction in methane flux was from mid latitude wetlands, arising from temperature and moisture mediated changes in emission rates.

Pinto and Khalil (1991) pointed out that changes in emissions rates of methane might well apply to emissions of other species as well (e.g., NO_x and CO), resulting in a stabilizing mechanism for OH levels during climate changes.

Predicting the response of the flux of methane from natural sources, such as wetlands, to future global warming is highly problematical. A good deal of attention has focused on the role of high latitude wetlands, because all general circulation models applied to the problem predict the largest temperature rises to occur at high latitudes. However, there are still substantial differences between model predictions regarding even the sign of changes in ground wetness in high latitudes. Although temperature plays an important role in determining the methane flux through the surface, ground wetness determines the direction of the flux. Observations in a high latitude wetland area around Hudson Bay, (Roulet and Moore, 1991) show a high degree of spatial variability in both magnitude and direction in the methane flux through the surface, with wetter soils acting as sources and drier soils acting as sinks for CH_4 . Uncertainties in future climate predictions therefore have consequences not only for the magnitude of any feedbacks in methane fluxes from wetlands but also for their direction.

4. Methane Control Strategies

Human activities that produce CH_4 as a byproduct are rice cultivation and cattle raising, natural gas production and

distribution and waste management. Hogan et al. (1991) have estimated that a reduction in agricultural and industrial emissions of CH_4 of only about 5 to 15% may be sufficient to stabilize its atmospheric level. Bruhl (1992) has considered different scenarios involving controls on emissions of NO_x and CO in his analysis. He estimated that stabilization of atmospheric CH_4 levels can be achieved with only a 5% reduction in its emissions, provided NO_x emissions are frozen at current levels along with a 20% reduction in CO emissions. For the case of NO_x and CO emissions, held constant at present values, a reduction in CH_4 emissions of about 9% is required. If anthropogenic CO emissions are held constant and anthropogenic NO_x sources are cut by 80% (corresponding to a reduction in total NO_x emissions of 40%), a reduction in CH_4 emissions of at least 15% is needed for stabilization (cf Rotmans, this volume). These results demonstrate the importance of considering interactions between chemical species in the atmosphere when developing control strategies. It should also be borne in mind, when reading these figures, that they are also subject to the same uncertainties discussed earlier with regard to model formulation. Possible measures for controlling CH_4 emissions are discussed in Harriss et al. (this volume) and Augenstein and Pacey (1992).

Controls on emissions of greenhouse gases should be viewed in the larger context of the tradeoffs involving the contributions of other greenhouse gases to global warming. The replacement of coal by natural gas results in a tradeoff of CO_2

emissions for CH₄ emissions. The energy yield of natural gas per kg CO₂ emitted is 1.64 times that for coal (Rodhe, 1990; Lelieveld et al., 1992). However, the favorable impact of a switch from coal to natural gas on total radiative forcing is offset by leakages during gas drilling and distribution. The break even point is at a gas leakage rate of about 5%. This value was estimated by using GWPs with short integration times, as the integration time increases the critical leakage rate also increases (Lelieveld et al., 1992). The average gas leakage rate is 2% or less in western industrialized countries with relatively new distribution systems and can range up to about 5% in areas with older distribution systems such as in the United Kingdom and in cities such as Paris and Brussels (C. Mitchell, pers. comm., 1991). A leakage rate of about 5% is also found in the Soviet Union (Andronova and Karol, 1992). Therefore, a switch from coal to gas in certain western areas may decrease radiative forcing associated with energy consumption, whereas a switch from coal to natural gas may actually increase radiative forcing in other areas. The consequences of a switch from coal to natural gas on atmospheric methane concentrations are discussed in Mitchell (1992) and Tie and Mroz (1992).

Tradeoffs involving issues other than global warming should also be included in discussions of CH₄ control strategies. A major question concerns the importance of CH₄ in the processes that affect stratospheric ozone depletion (Wuebbles and Tamareis, 1992). The photochemical oxidation of methane is a

major source of stratospheric water vapor. The condensation of water vapor in winter polar stratospheres is a key step in the formation of polar stratospheric clouds and hence in ozone hole formation. However, the reaction of methane with atomic chlorine is the major mechanism for recycling reactive chlorine into more stable reservoirs, such as HCl. It appears that the latter effect dominates, at least on a global scale, but more research is needed to further quantify this statement.

5. Research Needs

Several areas for further research were identified at the workshop. These include the use of satellites for mapping sources, techniques for deriving regional and global source inventories from measurements made over relatively small areas and the design of future monitoring networks. For example, Miller (1992) has described modeling the net flux of methane from regional biomes into the global scale. In addition, a rigorous intercomparison of tropospheric chemistry models is required to explain differences in OH predictions between models, (e.g.) shown in Table 1 and in general to better understand the response of these models to various perturbations. The development of coupled climate-chemistry models should also be encouraged for the calculation of Greenhouse Warming Potentials. Remote sensing, especially by satellites, has not been sufficiently utilized for its potential for gathering information about sources of methane. Instruments aboard satellites like SPOT and

LANDSAT could be especially useful for mapping wetlands. LANDSAT imaging has already proven useful for mapping the areal extent of biomass burning. UARS instruments (HALOE, ISAMS) are now measuring zonal variations in upper tropospheric methane. Data from these satellites may provide much needed information about zonal variations in major methane sources. This capability is currently lacking in existing surface based monitoring networks. It should also be noted that global scale chemical tracer models (e.g., Fung et al., 1991; Tie and Mroz, 1992) will be needed to help interpret the satellite data in terms of surface fluxes.

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TABLE 1. Model Calculated OH Values ($\times 10^{-6}$ molec/ cm^3)

<u>One Dimensional Models</u>	<u>Global Average</u>	<u>Surface Average</u>
Hemispheric		
MPI (Bruhl)	0.85	2.1
AREAL (Pinto)	0.59	1.2
OGI (Lu)	0.80	
Chemically Coherent Regions		
GSFC (Thompson)	0.60	
<u>Two Dimensional Models</u>		
LLNL (Wuebbles)	0.82	
CAM (Law)	0.95	1.6
<u>Three Dimensional Models</u>		
MPI (Kanakidou)	0.80	
	0.91 (zonally av. NO_x)	

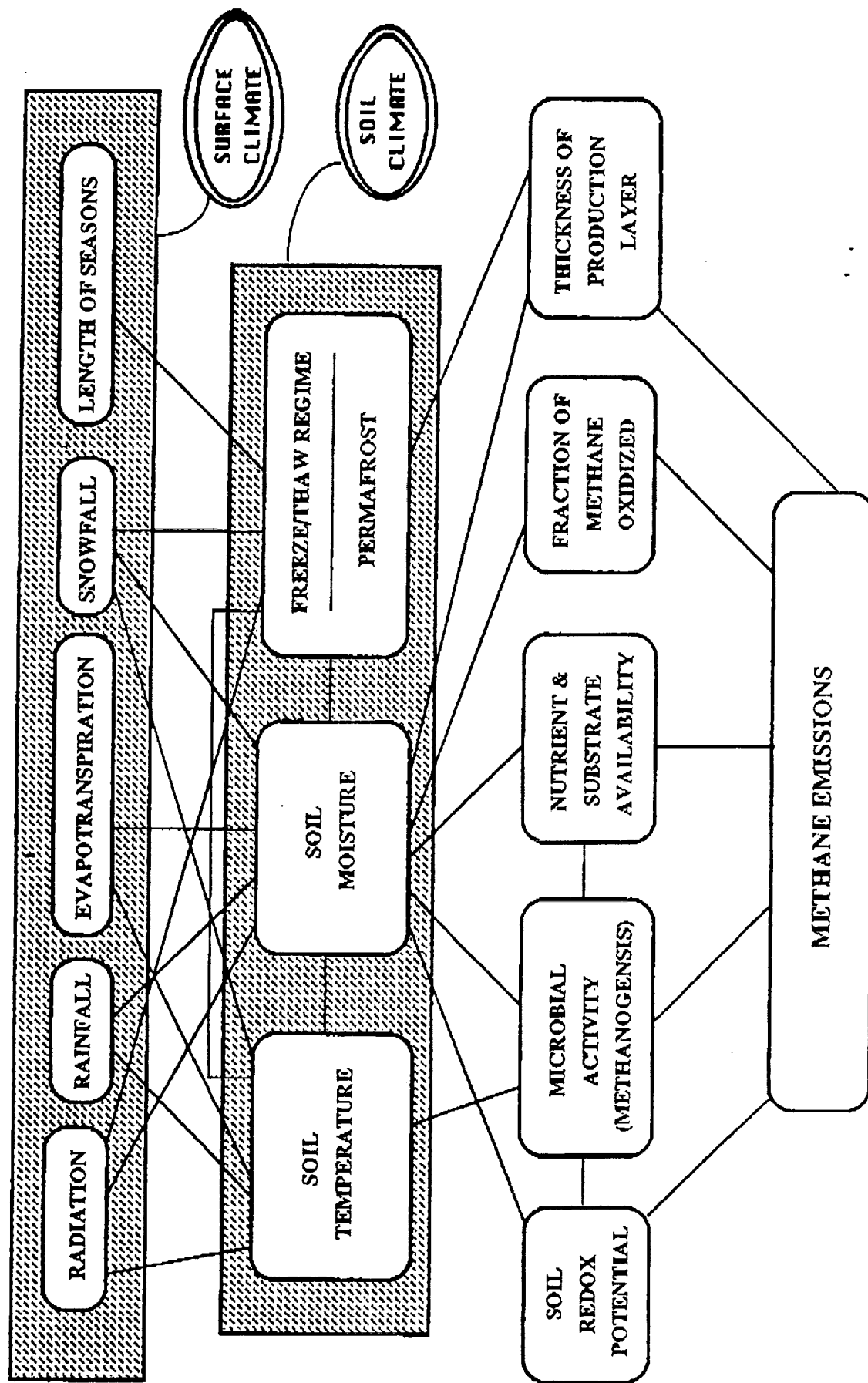


Figure 1